Characterization of Ni-Ti Shape Memory Alloys

Sheelan R. Areef*

Received on:25/6/2009
Accepted on:3/12/2009

Abstract

Master Samples NiTi (without additives) prepared using powder mixture of 55 wt% Ni and 45 wt% Ti by; mixing in a ball mill for two hours, then compacted at 300, 400, 500, 600, 700, and 800 Mpa, and then sintered at 950 ^{o}C for 9 hours under controlled atmosphere (argon). The same approach was made for the samples with Mo and Co additions compacted at 800 Mpa. From the results, it was found that compaction pressure has essential effect on; increasing hardness, decreases porosity percentage and corrosion rate. XRD test shows that the sintered samples are consisting of two phases martensite and austenite at room temperatures (mean thermal NiTi shape memory alloy). The Results shown that the hardness property and corrosion rate increased with all weight percentage of additives Mo and Co, and decreases porosity percentage.

خصائص سبائك ذاكرة الشكل Ni-Ti

الخلاصة

تم تحضير العينات الاساس NiTi (بدون الاضافات) باستخدام خليط من النيكل بنسبة وزنية 55% والتيتانيوم بنسبة وزنية 45% وتم خلطهما بطاحونة الكرات لمدة ساعتين وتم كبس الخليط عند ضغط كبس (300، 400،500،600، 700و800) ميكا بسكال وبعدها تمت عملية التلبيد عند درجة حرارة 950 ^{o}C ولمدة 9 ساعات بجو مسيطر عليه بغاز الاركون. استخدمت نفس الطريقة اعلاه لتحضير العينات مع الاضافات (Mo و Co)وتم كبسها عند 800 ميكا بسكال. من خلال النتائج وجد ان ضغط الكبس يؤثر بشكل اساسي على زيادة الصلادة وتقليل نسبة المسامية ومعدل التاكل. اختبار حيود الاشعة السينية يوضح بان العينات الملبدة تحتوي على طورين المارتنسايت والاوستنايت في درجة حرارة الغرفة (اي سبيكة ذاكرة الشكل الحرارية) كما اوضحت النتائج بان زيادة نسبة الاضافات تؤدي الى زيادة الصلادة ومعدل التاكل وتقلل من نسبة المسامية.

1. Introduction

Ni-Ti shape memory alloys belong to the group of materials known as "smart functional materials". The outstanding properties exhibited by them are the thermal shape memory effect. The alloy recovers it's programmed shape after heating above a specific temperature A_f (austenitic finish temperature) and superelastic (rubber-like) behavior (the alloy recovers its original shape after deformation to tensile strain as high as 8%). These properties are both based on thermo elastic, reversible martensitic transformation [1]. The high temperature austenite phase (with a body centred cubic structure) transforms martensitically upon cooling below an alloy specific temperature to a distorted monoclinic martensite structure. The NiTi shape

* Applied Science Department, University of Technology /Baghdad

https://doi.org/10.30684/etj.28.5.11
2412-0758/University of Technology-Iraq, Baghdad, Iraq

memory alloys usually consist of binary alloys with Ni and Ti concentration near an equiatomic composition. Other alloying elements like Fe, Cu and Nb may add in order to influence the transformation hysteresis behavior (shallower hysteresis for Fe and Cu, wider for Nb) as well as transformation temperatures and mechanical properties, particularly fatigue properties. Their microstructures are generally processed using complex [1-3]. Thermo mechanical treatments in order to obtain suitable properties such as thermal shape memory, superelasticity, all-round memory effect, and so on. These alloys are now being used in many biomedical applications, including orthodontic arch wires, stents, fillers, guide wires, catheter tubes, NiTi-osteo synthesis plates and staples, face and jaw surgical implants [1,4,5].

The aim of this work is to Produce thermal NiTi (a sample consisting of martenictic and austenitic phases at room temperature), by powder metallurgy approach and Studying the effect of Mo and Co addition on the hardness, porosity percentage and corrosion rate.

2.Experimental

2.1 Samples Preparation

Ni-Ti powder (master mixture; 55 wt% Ni with 45 wt% Ti) was prepared using a ball mill (Tire Jar Roll Drive with 2 inch Diameter and 24 inch long). by mixing for two hours. This mixture was used to prepare samples with 0.1, 0.2, and 0.3 wt% of Mo and Co additions. Table (1) shows the particle size and purity of each powder. After mixing, six master samples each weighing 5 grams, they were compacted at 300, 400, 500, 600, 700 and 800MPa respectively, by placing the powder in a die made from D2 tool steel with a diameter of 15mm. Samples with additions of 0.1, 0.2 and 0.3 wt% Mo and Co were also prepared and compacted at 800MPa.

Following the compaction, all of the samples were sintered at 950 °C for 9 hours (the samples were allowed to heat up with the heating rate 7°C/min) under argon atmosphere and were allowed to cool down at the furnace-cooling rate. The sintering process for all specimens has been done under controlled atmosphere (argon gas) to impede the samples oxidation. Following that, the samples were ground and polished.

2.2 Samples Testing

2.2.1 Corrosion test

Corrosion rate was measured for each sample by using the Corrosion Instrument (potentiostat /Galvanostat model 273A with frequency response detector model 1025) manufactured by priceton applied research where anodic and cathodic polarization curves were obtained using artificial saliva. Table (2) shows the Artificial saliva formulation as the electrolyte at 37°C with a scan rate of 5mV/sec and potential range of (-0.25-0.25 V), the exposed surface area (of the sample) to artificial saliva was 0.78 cm^2.

2.2.2 Vickers hardness

Vickers hardness was also measured where the average of 10 readings was

taken. All hardness values were taken at a load of 1Kg.

2.2.3 XRD test

The phases formed by sintering were detected using the XRD (X-Ray Diffractometer). The target used in the x-ray tube was Cu, therefore λcu = 1.542 °A for all of the samples.

2.2.4 Porosity percentage

The porosity percentage was also measured on the basis of density according to Eq. (1). For the master sample, the theoretical density is 6.5 $g/cm^{3.}$ [6] and the measured density of the sample is its weight divided by the volume (the samples are of a disc shape with a diameter of 15mm).

$$P\% = 1-(\rho_a/\rho_{th}) \times 100 \quad \ldots\ldots..(1)$$

Where:

P% : Porosity percentage

ρ_a : actual density

ρ_{th} : theoretical density

For the samples with additives, the theoretical density is:

$$r_o = (r_{Ni} \times at\%Ni) + (r_{Ti} \times at\%Ti) + (r_{additive} \times at\%additive) \quad \ldots\ldots (2)$$

3.Result and Discussion

XRD Pattern

All of the prepared master samples were compacted at various pressures and prepared samples (master with additives) were compacted at (800 MPa) and all of the samples were sintered at 950 °C for 9 hours. The sintering temperature used (950 °C) was about 0.8 of the melting temperature of the NiTi intermetallic compound (Tm =1310 °C), and holding that temperature for 9 hours under controlled argon atmosphere will result in complete sintering reaction due to the enhancement of the interdiffusion between Ti and Ni which in turn leads to an increase in the amount of NiTi phase produced and to a better shape memory effect. [7, 8].The phases produced as a result of the sintering process were investigated using the XRD technique. It is seen from Fig. (1-7) that there are no pure metals present, which proves that the sintering time and temperature used in this work result in complete sintering reaction [9]. The absence of any oxides is attributed to the controlled argon atmosphere used during the sintering process. Fig (1) Shows that the master sample compacted at 800 MPa consisted mainly of two phases the martensitic phase M (monoclinic) and the austenitic phase B2 (simple cubic) in addition to Ti_2Ni and Ni_3Ti. The formation of Ti_2Ni and Ni_3Ti might be attributed to the slow cooling of the samples with the furnace cooling rate whereas, in the sintering conditions used throughout this work, because of the Gibbs free energies for Ni_3Ti and Ti_2Ni were less than that for NiTi and it seems difficult to obtain a final equilibrium structure of NiTi alone just by solid - state diffusion, [10]. Mo and Co were added at a maximum percentage of (0.3 wt %) respectively, this is a very small amount to be detected by the XRD (as can be seen from the XRD patterns in Figs (2-7) because of their lower amount present.

Vickers Hardness

Hardness measurements were made for all of the samples, the hardness values were taken as the average of 10 random readings. Fig (8) Shows that as

the wt% of Mo and Co additions increased the measured hardness value will increase. This agrees with the fact that as the results in more elimination of pores is increased, the bonding between the particles is better (i.e. better interdifusion) which in turn leads to more pores elimination [11].

Porosity Percentages

Figure (9) shows that the porosity percentage decreases with increasing the additives (for each wt% of additives) and it is clear that the percentages of Mo added (0.1, 0.2, and 0.3wt%) have no significant influence on the porosity percentage when compared to the master but a small decrease in porosity could be observed with increasing Co addition from 0.1 to 0.2 to 0.3 wt% respectively (at 800 MPa) which could be attributed to the leads to close some pores [12].

Corrosion Rate Determination

Figure (10) indicates that the corrosion rate increase with increasing the wt% of Co and Mo, this can be attributed to the higher activity of additives compared to Ni, therefore, the Co and Mo acts as an anode to the Ni which in turn results in a reduction in the corrosion rate of Ni. The reason for the increase in the corrosion rate with increasing the wt% of additives added is due to the increase in the anodic area (Co &Mo), therefore, the Co and Mo is corroded more and the bulk is protected, But though the activity of Co and Mo is less than that of Ti, the Ti from a protective oxide film helps in keeping the corrosion rate not to influenced by the Co & Mo addition [13].

Conclusions

1. The samples sintered at 950ºC for 9 hours with 45 wt% Ti result in a two-phase structure (austenite and martensite) at room temperature. The samples with Co and Mo additions also resulted in the same two phase structure at room temperature.
2. Porosity percentage decreases with increasing the additives (for each wt% of additives)
3. The corrosion rate increases with increasing the wt% of Co and Mo.

References

[1].ASM Handbook, "Properties and selection Nonferrous Alloy and special Purpose Materials, Fifth edition, Vol. 2, (1998), pp. (897-901).

[2].GF. Andreasen & Fahl JL, "Shape Memory. In", Encyclopedia of medical devices and instrumentation, Volume 2.Wiley, New York, (1987), pp. (15-20).

[3].WJ. Buehler &Wang FE, "A summary of Recent Rsearch on the Nitinol Alloys and their potential Application in Engineering". Ocean Eng. 1, (1978), pp. (105-120).

[4].K. Shimizu &Tadaki T, "Shape Memory Effect Mechanism", Gordon and Breach Science, New York, (1978), pp. (1-60).

[5].V. N. Khodorenko et.al., "Exothermal and Endothermal Effects in Porous Titanium-Nickel Alloys", Institute of Medical Materials and Shape Memory Implants, Vol.27, No.22, (2001), pp. (80-85).

[6].T. W. Duerig et.al, "Engineering Aspects of Shape Memory Alloys", Butterworth-Heinemann, London (1990).
[7].Bing-Yun Li, Li-Liyi, " Shape Memory Effect of NiTi alloy", Chinese Academy of Sience, Vol. 42, February (1999) , pp. (96-97).
[8].Istvan Mihalcz "Fundamental characteristics and design method for nickel-titanium shape memory alloy" periodic polytechnic ser. Mechanical engneering.vol.45, No.1, (2001), pp. (75-86).
[9].Krone et al "The Potential of Powder Metallurgy for the Fabrication of Biomaterials", Advanced Engineering Materials, No.7, (2005), pp.(613-619)
[10].R.Hernandez et al. "Characteristics of Porous nickel-titanium alloy for medical applications" Bio-Medical Materials and Engineering, No.12, (2002), pp.(37-45).
[11].J.Y. Choi & S.Nemat Nasser "Effect of annealing and initial temperature on mechanical response of Ni-Ti-Cr shape-memory alloy" Materials Science Engineering, A 432, (2006), pp. (100-107)
[12].D.Cubela "The research of technological parameters influence on the process of nitinol fabrication and plastic deformation" Metalurgija Vol.45, No.1, (2006), pp. (61-66).
[13].S. p. Kedici, A. Abbas, "Corrosion Behavior of Dental Metals and Alloys in Didderent Media", Chemistry University of Ankara, (1998), pp. (800-808).

Table (1) purity and particle size of Ni, Ti, Mo and Co

Metal (Powder)	Purity (%)	Particle Size (μm)
Ni	99.9	6
Ti	99.5	75
Mo	98	25
Co	98.5	50

Table (2) Artificial saliva formulation

Component	Quantity (mM)
KH_2PO_4	2.5
Na_2HPO_4	2.4
$KHCO_3$	15
NaCl	10
$MgCl_2$	1.5
$CaCl_2$	1.5
Citric Acid	0.15

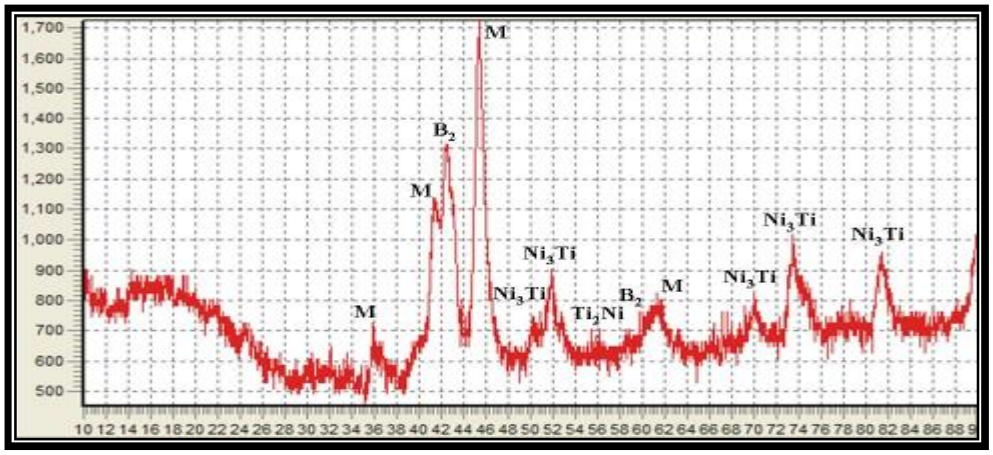


Figure (1) XRD pattern of a master sample pressed at 800MPa and sintered at 950°C for 9 hrs.

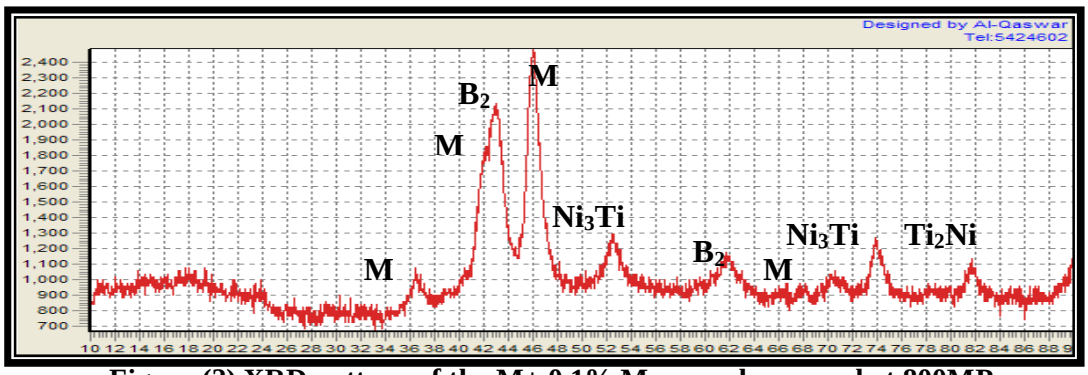
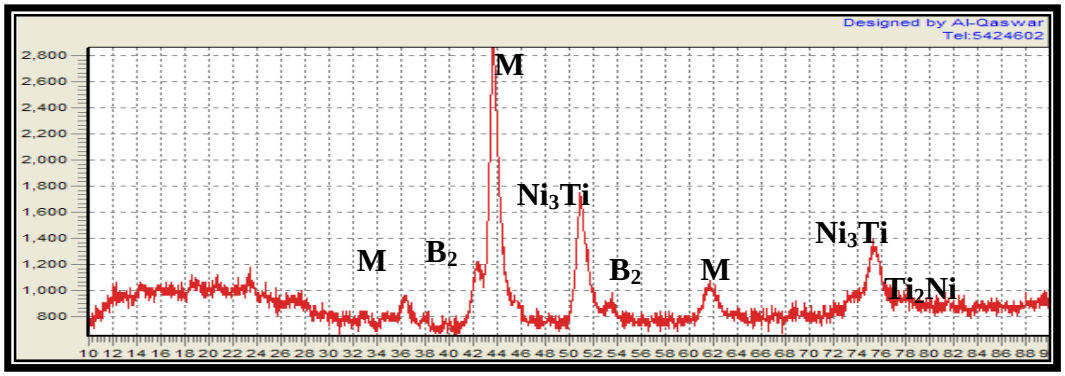


Figure (2) XRD pattern of the M+ 0.1% Mo sample pressed at 800MPa and sintered at 950°C for 9 hrs



Figure(3) XRD pattern of the M+ 0.2% Mo sample pressed at 800MPa and sintered at 950°C for 9 hrs

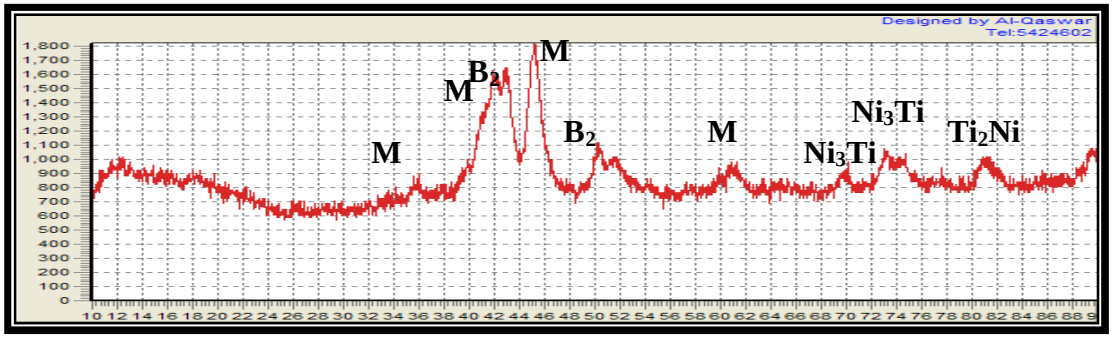


Figure (4) XRD pattern of the M+ 0.3% Mo sample pressed at 800MPa and sintered at 950°C for 9 hrs

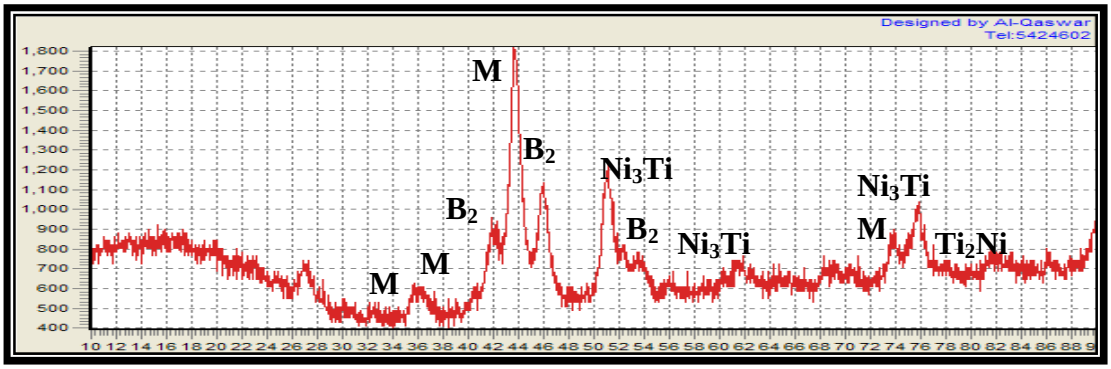


Figure (5) XRD pattern of the M+ 0.1% Co sample pressed at 800MPa and sintered at 950°C for 9 hrs

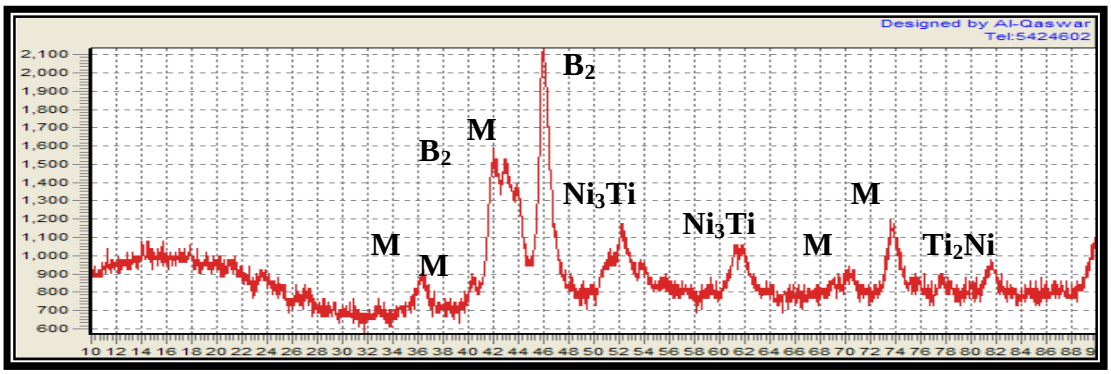


Figure (6) XRD pattern of the M+ 0.2% Co sample pressed at 800MPa and sintered at 950°C for 9 hrs

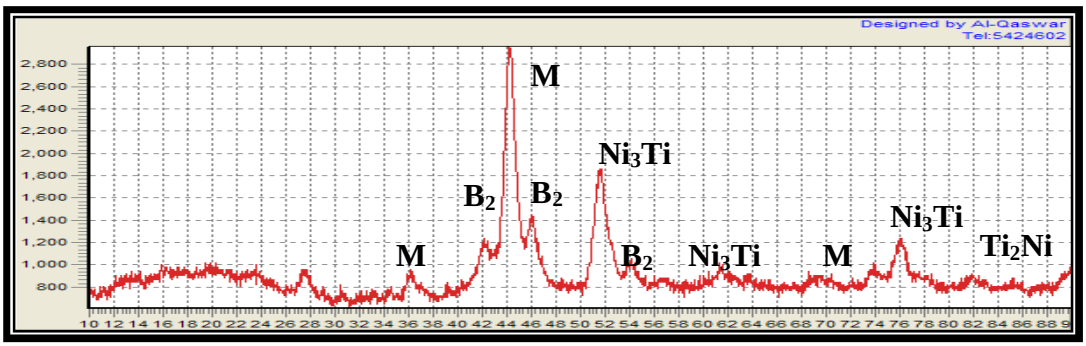


Figure (7) XRD pattern of the M+ 0.3% Co sample pressed at 800MPa and sintered at 950°C for 9 hrs.

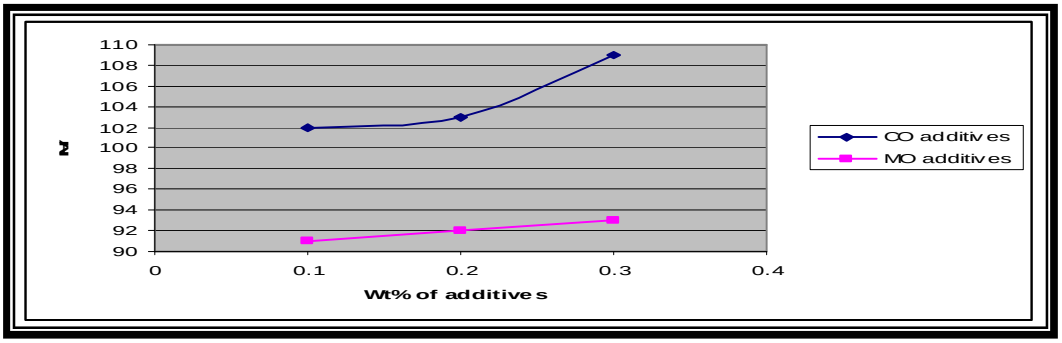


Figure (8) Vickers Hardness of the samples with various additives of Mo &Co pressed at800MPa and sintered at 950°C for 9 hrs

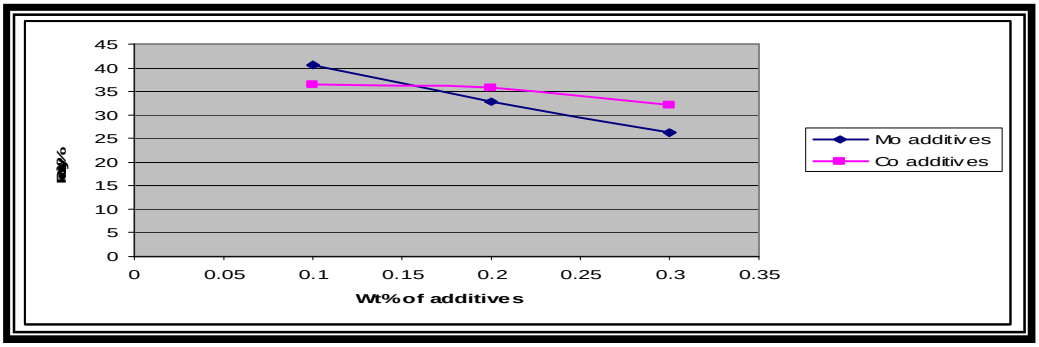


Figure (9) Porosity percentages of the samples with various additives of Mo &Co pressed at 800MPa and sintered at 950°C for 9 hrs.

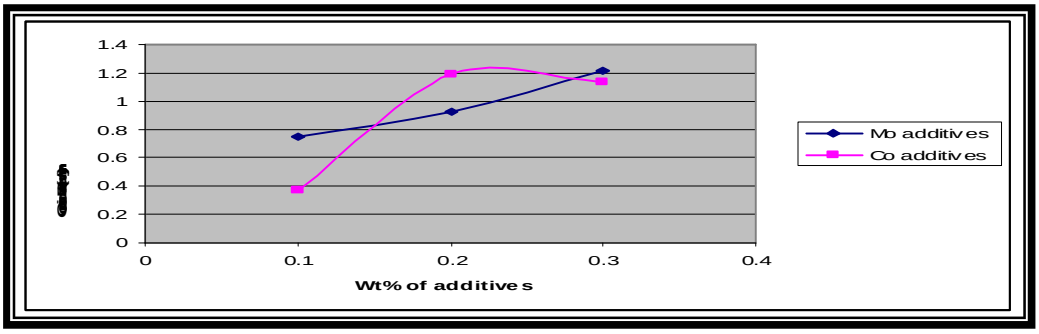


Figure (10) Corrosion rate (mm/yr) of the samples with various percentages of Mo & Co pressed at 800MPa and sintered at 950°C for 9 hrs